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Gas Sensors Based on Tin Dioxide for Exhaust Gas Application, modeling of response for pure gases and for mixtures

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Abstract

This paper concerns tin dioxide gas sensors for automotive exhaust gas application. It consists in elaborating robust sensors on alumina substrate by screen-printing technology. Sensors have been tested on a synthetic gas bench which is able to generate high gas velocity and gases at high temperatures close to real exhaust gas conditions. The responses of the sensors to three gases were modeled, and the classical model of electrical conductivity with one reducing or oxidizing pollutant gas was extended to mixtures. Comparisons between models and experiments are presented with good agreements.

gas sensors; tin dioxide; exhaust gas; gas mixture; model

1. Motivation and sensors

Legislation obliges car manufacturers to reduce and control emissions. Hence, there are actually many researches on exhaust gas sensors. Most of them are based on devices issued from oxygen Lambda sensors or mixed potential type sensors [1,2] using solid electrolyte as sensing element. On the contrary, there are few studies on this topic, using semiconducting metal oxides gas sensors. This kind of gas sensors, in particular tin dioxide sensors, is well known and is used in many areas such as, for example, process control, environmental control and domestic security [3]. So, in this study, we developed a robust

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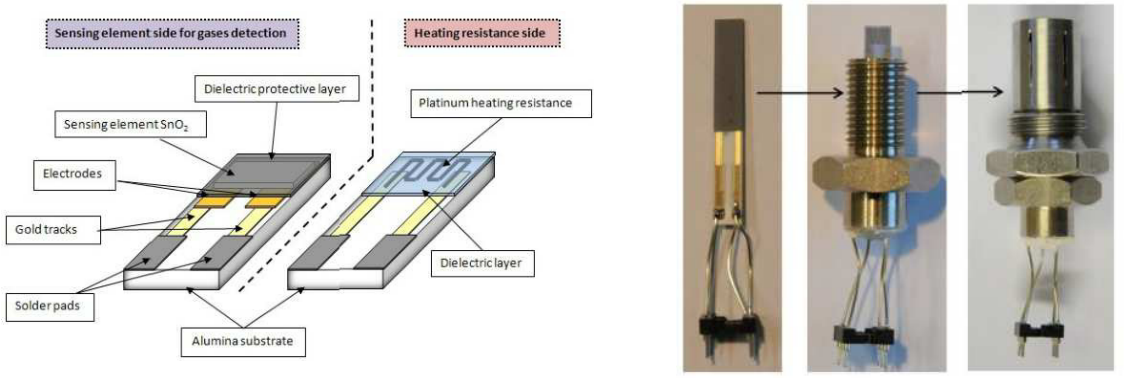
gas sensor based on tin dioxide, and we investigated its potentialities for automotive exhaust gas application.

We opted for robust planar sensors on alumina substrate which were totally elaborated by screen-printing technology. Sensors consist in an encapsulated sensitive layer of tin dioxide, with gold electrodes, surmounted by a porous protective layer based on a dielectric material. An integrated platinum heater is deposited on the opposite side of the substrate (fig 1). More than 100 sensors were realized and tested, so that the results have a suitable statistical weight.



(a) (b)

Fig. 1. Tin Dioxide sensors (a) schematic view; (b) without and with encapsulation

Sensors were tested in a laboratory testing bench with conditions close to those of an automotive exhaust pipe. Our “standard conditions” were: gas velocity 0 to 6 m/s, gas temperature 20 to 250°C, 2 vol.% of water vapor, 12 vol.% of oxygen. The temperature of the sensors was within the range 400°C-600°C and was controlled. The detected "pollutant" gases were carbon monoxide (CO), nitrogen dioxide (NO_2) and propane (C_3H_8). The electric conductances were measured with one "pollutant" gas and with binary mixtures.

Our measurements have showed that the gas temperature and velocity had no influence on the sensors responses , when their temperature is controlled. On the other hand, the sensitivity depends on the temperature of the sensor: it is maximal at 400, 500 and 600°C respectively for CO, C_3H_8 and NO_2.

2. Modeling of the sensors responses

2.1. One pollutant

It is now relatively well admitted that the electric conductivity of tin dioxide is governed by the depletion phenomena at the grain boundaries, linked to oxygen species (O^- ions) adsorbed at the surface. N. Yamazoe and K. Shimanoe [4] in particular, modeled the consequences of the presence of a polluting gas on this conductivity. Molecules of a reducing gas A (like CO or C_3H_8) are oxidized by O^- ions, that reduces their number and thus increases the conductivity. They show that in the case of these gases and for the adequate approximations, the conductance follows a ½ power function:

$$G_A = G_0 \times (1 + K_A \times P_A)^{1/2} \quad (1)$$

where G_0 is the electric conductance with our previously defined "standard conditions" and P_A is the partial pressure of A. Then the resistance can be written:

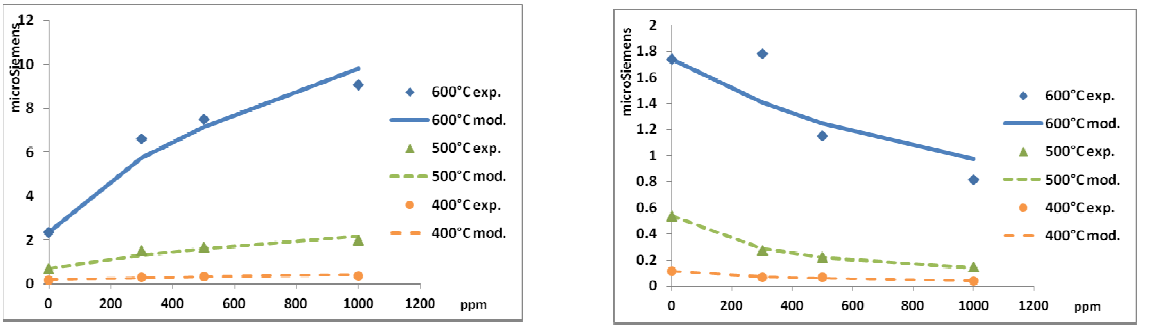
(2)

Oxidizing molecules C, like nitrogen dioxide behaves in a different way: they are adsorbed in the form of anions, in a not competitive way with O^-, which has for consequence an increase of the tin dioxide resistance, according to following law:

(3)

where R_0 is the electric resistance in "standard conditions" and P_C is the partial pressure of C.

Tests at various temperatures of the sensors for reducing (CO, C_3H_8 (fig 2a)) or oxidizing pollutants (NO_2: fig 2b) show that our sensors responses are well fitted with previous model. Hence for each temperature, it is possible to determine the model constant "K" for a given gas.



(a) (b)

Fig. 2: Variations of sensors conductance (µS) with: (a) propane (experiments and 1/2 power law models); (b) nitrogen dioxide (experiments and -1 power law models)

2.2. Mixtures of 2 pollutants

In the case of a mixture of two reducing gases A and B, we can consider that we have the same phenomena for both gases, but in a not competitive way because of a low fractional surface coverage if we consider low gas concentration (lower than 1000ppm). Then we can propose the following model of conductance:

(4)

The case of a gas mixture containing at the same time a reducing gas A and an oxidizing gas C, other than oxygen, is more complex. We saw that the oxidizing gas adsorbs independently on the oxygen and on other preadsorbed gases on SnO_2, with the hypothesis of low fractional surface coverage of O^-. The contribution of the oxidizing gas in the increase of resistance is thus the term K_CP_C of equation (3) which depends only on the concentration of the oxidizing gas C, and which is added to the initial resistance, R_0 if there is no other adsorbed gas ("standard" conditions) or R_A given by equation (2) if a reducing gas is also present in the system.

Hence, we can represent the electric resistance of the sensors in mixture reducer / oxidizer by the serialization of the resistance under reducing gas R_A (equation 2) and the resistance term due to the influence of the oxidizing gas $K_C P_C$ in equation (3), independently on the other present gases. As a result, we can suggest the following electrical model to quantify the electrical resistance in a reducing/oxidizing mixture :

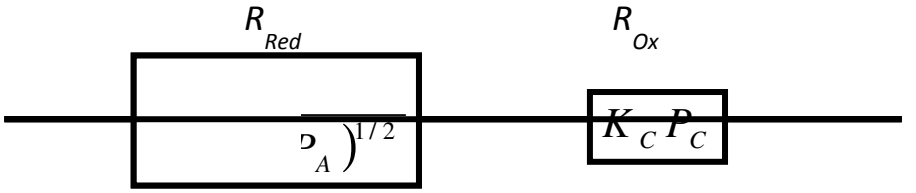
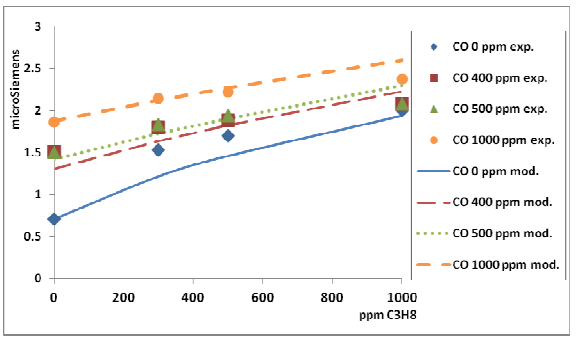


Fig 3: Electrical model of tin dioxide resistance for a reducing / oxidizing mixture

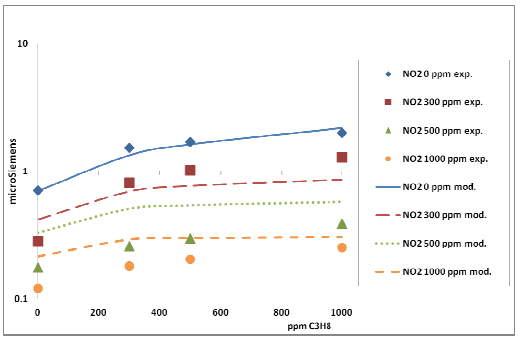
Then the expressions of resistance and conductance are:

———— and – ———————— (4)

Tests with sensors at 500°C and with a mixture of two reducing gases (CO and C_3H_8 (fig 4a)) or a mixture reducing and oxidizing gases (C_3H_8 and NO_2: fig 4b) show that this model is satisfactory, contrary to others tested. From both equation (4) and from experimental results, we can notice that the sensibility to a reducing gas decreases (slope change in fig. 4b) with increasing oxidizing gas concentration. Extremely, for high enough oxidizing gas partial pressures, the conductance of the sensors becomes independent on the reducing gas concentration.



(a)



(b)

Fig. 4. Sensors conductance (µS) with mixtures at 500°C, comparison between experiments and mixture models (a) carbon monoxide and propane; (b) nitrogen dioxide and propane

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